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Introduction

Quality assurance (QA) is a system of activities and processes put in place to assure that monitoring and measurement data meet user requirements. Quality Control (QC) consists of procedures used to verify that prescribed standards of performance in the monitoring and measurement process are attained. Quality assurance requirements for environmental monitoring of DOE facilities are mandated by DOE orders and guidance. DOE Order 5400.1 identifies QA requirements for radiological effluent and surveillance monitoring and specifies that a QA program consistent with DOE Order 5700.6 be established. The latter order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality achievement in DOE programs. The DOE Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance (U.S. Department of Energy 1991) requires the preparation of an Environmental Monitoring Plan containing a QA section discussing the applicable elements of the American National Standards Institute/American Society of Mechanical Engineers (ANSI/ASME) NQA-1, Quality Assurance Program Requirements for Nuclear Facilities (ASME 1989).

LLNL conducted QA activities in 1994 at the Livermore site and Site 300 in accordance with a plan based on DOE Order 5700.6C (Garcia and Failor 1993). DOE Order 5700.6C prescribes a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity, maximizing the effectiveness and efficiency in resource use.

LLNL environmental sampling is conducted according to procedures published in an appendix to the LLNL *Environmental Monitoring Plan* (Tate et al. 1995). Environmental monitoring samples are analyzed by LLNL or commercial laboratories using EPA standard methods when available. When EPA standard methods are not available, custom analytical procedures, usually developed at LLNL, are used. The radiochemical methods used by LLNL laboratories are described in each laboratory's procedures. When analyses are performed by independent contractors, LLNL requires that their laboratories be certified by the State of California for the analyses performed for LLNL. In addition, LLNL requires all analytical laboratories to maintain adequate quality assurance programs and documentation of methods.

Quality Assurance Activities

The LLNL environmental monitoring program was audited successfully by the Department of Energy (EH-24) and the Defense Nuclear Facility Safety Board in 1994.

An intergroup forum was established within the Environmental Protection Department (EPD) to address issues with contract analytical laboratories. Several issues were resolved, including development of a shipping protocol for environmental samples, resolution of electronic data transfer issues, resolution of an apparent bottle contamination problem, and identification of a laboratory with the capability of providing one type of analysis that the contracted laboratories previously had been unable to perform adequately. One of five contract analytical laboratories used by the environmental monitoring program was audited by EPD personnel in 1994, and audits of the remaining four laboratories are planned for 1995. A formal program for review of laboratory quality control data was also initiated, and LLNL began a program in which quarterly performance evaluation samples are sent to its contract analytical laboratories.

During 1994, 181 Nonconformance Reports (NCRs) were written. The major sources of NCRs were failure of air particulate sampling equipment and analytical laboratory problems. Air particulate sampling equipment problems are ongoing and cannot be eliminated without a major resource expenditure for upgraded equipment. Analytical laboratory issues are being addressed as they arise.

In September 1994, a nationally recognized expert in environmental monitoring was brought to LLNL to give a two-day training to environmental monitoring personnel. This training included basic environmental sampling and analysis techniques, quality control and quality assurance, and an introduction to data quality objectives.

Participation in Laboratory Intercomparison Studies

During 1994, LLNL's Radiation Analytical Sciences (RAS) laboratory and the Hazards Control Department analytical laboratory (HCAL) both participated in the EPA's Environmental Monitoring Systems Laboratory (EMSL) Intercomparison Studies Program. All eight samples analyzed by HCAL fell within the control limits provided by EMSL. Two of 11 samples analyzed by RAS gave unacceptable results. One was due to an error in data reduction; the other was due to startup errors for a new analysis method.

HCAL participated in four California Department of Health Services Environmental Laboratory Accreditation Program (ELAP) water pollution studies for metals during 1994. One of 70 analyses fell outside of acceptable limits for this program because of a zinc contamination problem at the laboratory, which has been resolved.

RAS also participated in the 1994 intercomparison studies by the DOE Environmental Measurements Laboratory for various radionuclides on air filters and in soil, vegetation, and water. Ten of 52 analyses fell outside of acceptable limits. Two were due to calculation errors, two were due to reporting the wrong exponent value for results presented in scientific notation, and four were due to a problem with plutonium that is still under investigation.

The potential effects of unacceptable intercomparison study results on routine data have not been determined or evaluated. It has been recommended that the EPD group currently focusing on quality control results from analytical laboratories assume the responsibility for this investigation and begin to develop a better understanding of intercomparison study results during 1995.

The results of all of these intercomparison studies are presented in Volume 2. Contract laboratories are also required to participate in laboratory intercomparison programs; however, permission to publish their results for comparison purposes has not been granted.

Duplicate Analyses

Tables 14-1 through **14-3** present data generated by duplicate samples submitted to the same analytical laboratory, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 14-1** and **14-2** contain data pairs with both values above the detection limit and all radiological results for which a reported value was available. They exclude radiological values for which only a minimum detectable activity was reported. In addition, **Table 14-2** excludes radiological results for which the reported value was negative. **Table 14-3** contains data pairs with either or both values below the detection limit.

If there are more than eight data pairs with both results above the detection limit, precision and regression analyses are performed; the results are presented in **Table 14-1**. Precision is measured by the percent relative standard deviation [%RSD; see the EPA *Data Quality Objectives for Remedial Response Activities: Development Process*, Section 4.6 (U.S. Environmental Protection Agency 1987)]. Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method; however, values above 30% are common. The results for %RSD given in **Table 14-1** are the 75th percentile of the distribution of individual precision values. Regression analysis consists of fitting a straight line to the duplicate-routine pairs, as illustrated in **Figure 14-1**. Good agreement between the duplicate and routine samples is indicated when the data lie close to a line with slope equal to one and intercept equal to zero. Allowing for normal analytical variation, the slope of the line should be between 0.7 and 1.3, and the intercept should be within \pm the detection limit. The coefficient of determination (r^2) should be >0.8 .

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Table 14-1. Quality assurance duplicate sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit.

Media	Analyte	Units	N ^(a)	% RSD ^(b)	Intercept	Slope	r ²
Air	Beryllium ^(c)	pg/m ³	11	23.1	1.50	0.733	0.28
	Gross alpha ^(d)	pCi/L	97	121.	-4.26×10^{-8}	0.933	0.090
	Gross beta	pCi/L	97	29.5	-7.36×10^{-7}	0.976	0.83
	Tritium ^(c)	pCi/L	35	23.2	-0.00048	1.22	0.67
Building Drain Investigation	Copper ^(c)	mg/L	10	38.2	0.118	1.32	0.57
	Zinc	mg/L	9	59.1	0.0540	0.934	0.93
Radiation dose	Rad dose ^(c)	mrem	50	2.40	-0.165	1.01	0.67
Ground water	Arsenic	mg/L	38	5.94	-0.0009	1.03	0.98
	Bicarbonate alkalinity (as CaCO ₃)	mg/L	12	5.50	-16.8	1.10	0.76
	Calcium	mg/L	14	3.63	1.38	0.988	1.0
	Chloride	mg/L	13	2.48	-3.32	1.02	1.0
	Fluoride	mg/L	12	2.92	0.0215	0.945	0.99
	Gross alpha ^(d)	pCi/L	8	112	1.18	0.349	0.12
	Gross beta ^(d)	pCi/L	13	40.9	1.30	0.813	0.34
	Magnesium	mg/L	14	3.14	-0.125	1.02	0.99
	Nitrate (as N)	mg/L	9	6.73	0.558	0.917	0.97
	Potassium	mg/L	13	4.88	-0.208	1.00	0.99
	Radium-226 ^(c)	pCi/L	15	67.0	0.334	-0.0219	0.031
	Selenium	mg/L	19	5.89	-0.00105	1.11	0.86
	Sodium	mg/L	13	3.04	1.79	0.998	1.0
	Specific conductance	μmhos/cm	52	3.55	-47.9	1.07	0.99
	Sulfate	mg/L	13	4.22	-1.08	0.999	1.0
	TDS	mg/L	39	5.44	-10.6	1.02	0.99
	TOC ^(d)	mg/L	16	84.9	2.91	0.0419	0.0031
	TOX ^(d)	mg/L	19	79.8	0.0403	0.240	0.17
	Total alkalinity (as CaCO ₃)	mg/L	12	5.50	-16.8	1.10	0.76
	Total hardness (as CaCO ₃)	mg/L	15	4.04	-50.0	1.17	0.86
	Tritium ^(c)	pCi/L	9	14.9	6,250	-0.0101	0.0063
	Uranium-234, Uranium-233 ^(c)	pCi/L	16	53.3	-0.426	1.29	0.93
	Uranium-235, Uranium-236 ^(d)	pCi/L	15	81.2	-0.368	6.30	0.14
	Uranium-238	pCi/L	16	50.9	-0.275	1.30	0.97
	pH	Units	50	0.962	-0.0865	1.01	0.67

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Table 14-1. Quality assurance duplicate sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit (concluded).

Media	Analyte	Units	N ^(a)	% RSD ^(b)	Intercept	Slope	r ²
Sewer	Gross alpha ^(d)	pCi/L	45	126	-0.617	1.42	0.40
	Gross beta	pCi/L	45	17.7	-1.66	1.10	0.80
	Tritium	pCi/L	44	82.6	0.829	0.908	0.93

^a Number of duplicate pairs included in analysis.

^b 75th percentile of percent relative standard deviation (%RSD), where $\%RSD = \left(\frac{200}{\sqrt{2}} \right) \left(\frac{|x_1 - x_2|}{(x_1 + x_2)} \right)$ and x_1 and x_2 are the reported concentrations of each routine-duplicate pair.

^c Outside acceptable range of slope or r² due to outliers.

^d Outside acceptable range of slope or r² due to variability.

Table 14-2. Quality assurance duplicate sampling. Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit.

Media	Analyte	N ^(a)	Mean Ratio	Minimum Ratio	Maximum Ratio
Air	Plutonium-239	5	1.1	0.29	2.4
Ground water	Chromium	7	0.99	0.83	1.2
	Thorium-228	6	1.6 ^(b)	0.53	4.5
	Thorium-232	5	0.81	0.015	1.8
	Tritium	2	0.86	0.74	0.98
Rain	Gross alpha	4	1.2	0.22	2.8
Runoff (from rain)	Gross beta	4	1.1	0.85	1.5
	Tritium	1	1.1	1.1	1.1
Soil	Beryllium	2	0.95	0.86	1.0
	Cesium-137	3	1.3	0.94	1.8
	Plutonium-239	3	0.77	0.006608	1.3
Surface water (e.g., ponds, streams)	Tritium	7	0.98	0.81	1.2
Vegetation	Tritium	6	0.76	0.14	1.0
	Tritium, per gram dry weight	6	0.62 ^(b)	0.089	1.1

^a Number of data pairs.

^b Outside acceptable range of 0.7–1.3.

Table 14-3. Quality assurance duplicate sampling. Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Media	Analyte	Number of Inconsistent Pairs	Number of Pairs	Percent of Inconsistent Pairs
Air	Beryllium	1	13	7.69
	Plutonium-239	1	7	14.29
Building Drain Investigation	Aluminum	1	8	12.5
	Barium	1	9	11.11
	Chloroform	1	5	20
	Copper	2	6	33.33
	Iron	1	7	14.29
	Lead	1	7	14.29
	Methylene chloride	3	5	60
	Silver	1	13	7.69
	Zinc	1	7	14.29
Ground water	Antimony	1	4	25
	Lead	1	33	3.03
	TOC	1	4	25
	Tritium	1	19	5.26
Vegetation	Tritium	1	6	16.67
	Tritium, per gram dry weight	1	6	16.67

If there are eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs are averaged; the average, minimum, and maximum ratios for selected analytes are given in **Table 14-2**. The average ratio should be between 0.7 and 1.3.

If one of the results in a pair is below the detection limit, then the other result should be less than two times the detection limit. **Table 14-3** identifies the sample media and analytes for which at least one pair failed this criterion. Analytes with fewer than four pairs total are omitted from the table.

These analyses show generally good agreement between routine samples and quality assurance duplicates: approximately 75% of the pairs have a precision better than 30%. Data pairs that do not fall into this area of precision generally fall into one of two categories. The first category, outliers, can occur due to data transcription errors, measurement errors, or real but anomalous results. Of 35 data sets reported in **Table 14-1**, seven did not meet the criterion for acceptability due to outliers. The other category of results that does not meet the

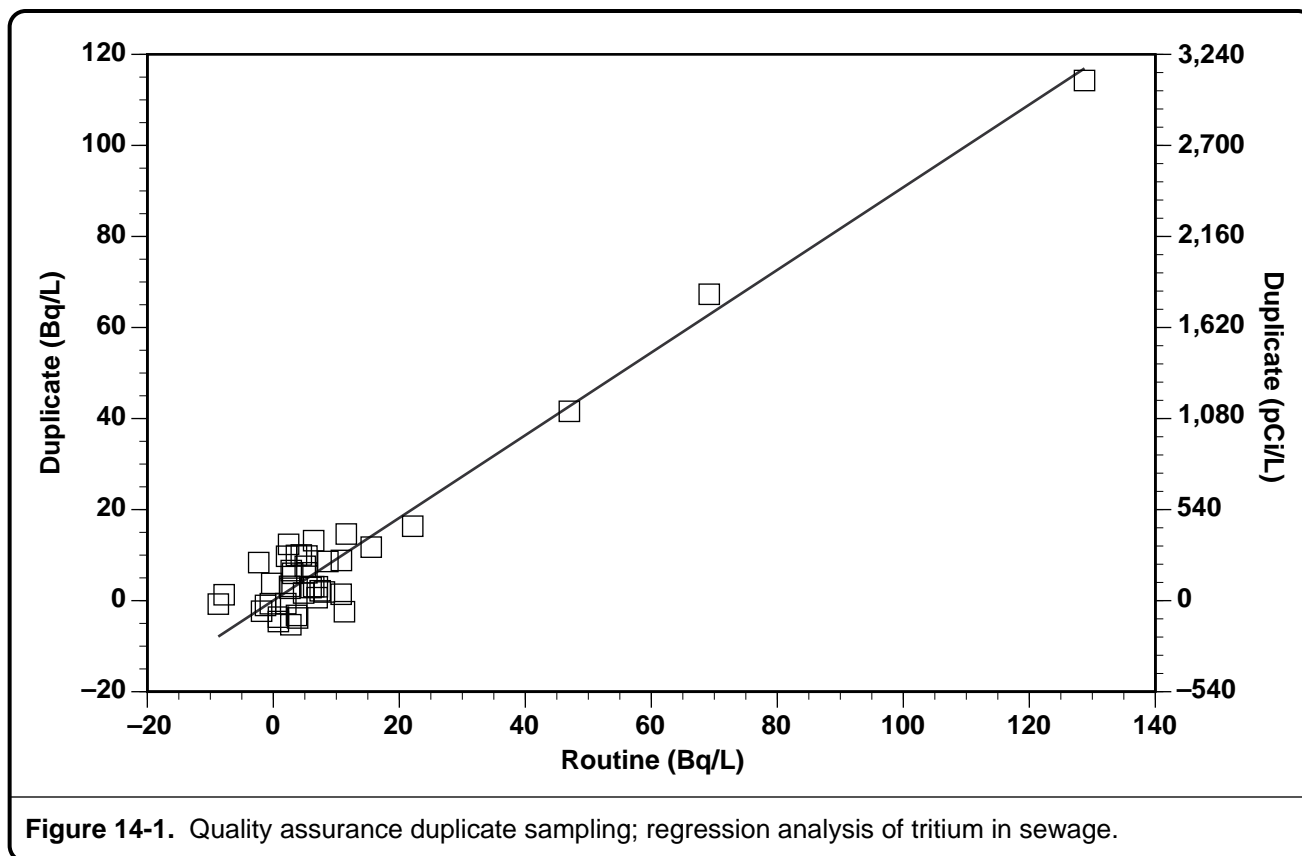


Figure 14-1. Quality assurance duplicate sampling; regression analysis of tritium in sewage.

criterion for acceptability consists of data sets in which there is a lot of scatter. This tends to be a problem for measurements at extremely low concentrations in general. Low concentrations of particulates in air highlight this effect even more because one or two particles on an air filter can significantly impact results. Another cause of high variability is sampling and analytical methodology. Analyses of total organic carbon and total organic halides are particularly difficult to control. Of the 35 data sets in **Table 14-1**, seven show sufficient variability in results to make them fall outside of the acceptable range.

Quality assurance duplicates may also be used to identify errors—for example, mislabeled samples and data entry errors. Less than one percent of the samples involved in the duplicate sampling regime appear to have errors of this kind. This indicates that we have maintained a high standard of sample handling and data management.

Deviations and Changes to the Sampling Program

Changes to the environmental sampling effort made during 1994, deviations from planned environmental sampling, and regularly scheduled samples for which data are not reported because they could not be collected or were lost during analysis are summarized below.

Changes to Environmental Monitoring Networks

Changes that were made to environmental monitoring networks in 1994 are summarized in **Table 14-4**. One air particulate and air tritium monitoring location (L-LCCY) was eliminated during 1994 because of continued vandalism of sampling equipment at that locations. Minor changes in locations were made to the rain and arroyo sediment monitoring networks to more effectively monitor LLNL's impact on the environment based on technical review of those monitoring networks. Two new monitoring networks were added in 1994. Compliance monitoring at Site 300 was added for storm water runoff and for cooling tower water.

The LLNL environmental monitoring program uses alpha-numeric location designator codes to define sampling locations. Volume 2 includes tables that decode these sampling location designators and provide a cross-reference between current designators and those used in previous years. Changes made in 1994 are noted on those tables.

Table 14-4. Changes to environmental monitoring networks in 1994.

Environmental Medium	Livermore Site	Site 300
Air particulate	Abandoned location L-LCCY	No changes made in 1994
Air tritium	Abandoned location L-LCCY	No changes made in 1994
Soil	No changes made in 1994	No changes made in 1994
Arroyo sediment	Abandoned locations L-438E, L-4THA, L-ALPN, and L-ALPW , and added location L-ESB in 1994	No changes made in 1994
Vegetation	Added location L-GRD	No changes made in 1994
Milk	Abandoned after 1993	—
Honey	Abandoned after 1993	—
Wine	No changes made in 1994	—
Rain	Added location L-VET	No changes made in 1994
Storm water runoff	Added location L-CDBX	Monitoring began in 1994
Drainage Retention Basin	No changes made in 1994	—
Other surface water	No changes made in 1994	—
Ground water	—	No changes made in 1994
Cooling towers	—	Monitoring began in 1994
Sewage	No changes made in 1994	—
Thermoluminescent dosimeters	No changes made in 1994	No changes made in 1994
Neutrons	1994 results not reported due to equipment/calibration problems	—

Explanation of Missing Samples

Planned samples and actual samples collected and analyzed in 1994 are summarized in **Table 14-5**. With the exception of the storm-water runoff network, the Drainage Retention Basin, and neutron monitoring, the levels of completeness for networks that were reported previously are similar to historical levels.

Table 14-5. Sampling completeness in 1994, Livermore site and Site 300.

Environmental Medium	Samples Planned	Samples Analyzed	Completeness
Air particulate	1664	1568	94%
Air tritium	494	463	94%
Soil	46	46	100%
Arroyo sediment	46	45	98%
Vegetation	94	92	98%
Wine	25	25	100%
Rain	87	87	100%
Storm water runoff	36	25	69%
Drainage Retention Basin	312	228	73%
Other surface water	70	70	100%
Ground water	2155	2153	99.9%
Sewage	653	631	97%
Thermoluminescent dosimeters	397	373	94%
Neutron monitors	32	0	0%
Cooling towers	49	36	73%

A drop in completeness occurred for the storm water runoff network because samples planned for late 1994 (the beginning of the rainy season) could not be taken because no storm occurred that generated enough runoff for sampling during that period. Several weekly drainage retention basin samples were overlooked by sampling technologists during 1994, leading to diminished sampling completeness for that network. This training issue has been addressed. Neutron monitoring results for 1994 were not presented because the REM meters were found to be seriously out of calibration due to age-related deterioration. This monitoring network was eliminated at the end of 1994 (see Chapter 11). See Volume 2 for additional discussion about missed samples.

The one new sampling network for 1994, Site 300 Cooling Towers, also exhibited relatively low completeness. This was due to sampling startup errors and difficulties in accessing the cooling towers.

Statistical Methods

Statistical methods used in this report have been implemented pursuant to the *Environmental Monitoring Plan* (Tate et al. 1995). These methods reduce the large volumes of monitoring data to summary concentration estimates that are suitable for both temporal and spatial comparisons. Attention is given to estimating accuracy, bias, and precision of all data.

Data review and analyses are conducted in accordance with the *Environmental Monitoring Plan* and the Environmental Monitoring Section's Data Analysis Procedure. These documents contain detailed information regarding the acceptability of data and the procedures that are followed for the identification, notification, and correction of suspect data.

Radiological Data

The precision of radiological analytical results is displayed in the data tables as the 2σ counting error. The counting errors are not used in any summary statistic calculations. By convention, any radiological result exhibiting a 2σ counting error greater than 100% is said to be below the detection criterion and is presented in the tables with a less-than symbol (<) to indicate its status. No value of error is reported for values below the detection criterion. The reported concentration is derived from the number of sample counts minus the number of background counts. A sample with a low or zero concentration may therefore be reported to have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons. Some analytical laboratory reports provide a minimum detectable activity rather than a reported value when the radiological result is below the detection criterion.

Nonradiological Data

Nonradiological data that are reported as being below the analytical detection limit also are displayed in the tables with a less-than symbol. The actual detection limit values are used in the calculation of summary statistics as explained below.

Statistical Comparisons

Standard comparison techniques (such as regression, t -tests, and analysis of variance) have been used where appropriate to determine the statistical significance of trends or differences between means. All such tests of significance have been performed at the 0.05 level. When such a comparison is made, it is explicitly stated in the text as being "statistically significant" or "not statistically significant." Other uses of the word "significant" in the text do not imply that statistical tests have been performed. These uses instead relate to the concept of practical significance and are based on professional judgment.

Summary Statistics

Determinations of measures of central tendency and associated measures of dispersion are calculated according to Environmental Monitoring Section's Data Analysis Procedure. For data sets not containing values below the detection criterion, the measure of central tendency and dispersion are the median and interquartile range (IQR). The IQR is the range that encompasses the middle 50% of the data set.

For data sets with one or more, but fewer than one half, values below the detection criterion, the measure of central tendency is the median. If the values of the detection limits and the number of values below the detection limit permit (determined on a case-by-case basis), dispersion is reported as the IQR. Otherwise, no measure of dispersion is reported. Statistics are calculated using the reported detection limit value for nonradiological data or the reported value for radiological data.

For data sets with one half or more of the values below the detection criterion, the central tendency is reported as less than the median value. Dispersion is not reported.

Radiation Units

Data for 1994 have been reported in Système Internationale (SI) units to conform with standard scientific practices and federal law. Values in the text are reported in becquerels (Bq) and millisieverts (mSv); equivalent values in picocuries (pCi) and millirems (mrem) are given in parentheses.